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Electronic and vibrational spectra of some chlorinated pyridinols

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Abstract: This paper confines in reporting the investigations of the vapour absorption spectra of 5-chloro-2-Pyridinol and 2-Chloro-3-Pyridinol in the ultraviolet region and the infrared absorption spectra in the 400-4000 cm^{-1} region KBr phase Strong bands at 2917.9A (34261 cm^{-1}) and 2829.6A (35330 cm^{-1}) in the electronic spectra of the two molecules have been identified as the 0, 0 band. On the basis of the red shift together with the strong appearance of the ν_1 mode it has been concluded that in each case the electronic transition in question is $\pi-\pi$ one. The electronic absorption spectra of each molecule have been analysed in terms of several ground and excited state fundamental vibrational frequencies. The infrared absorption spectra of the two molecules have been analysed in terms of fundamentals their combinations and overtones. The assignment of the fundamental frequencies of the ultraviolet and infrared spectra to the probable modes of vibration have also been made.

1. Introduction

The electronic spectra of pyridine has been analysed in terms of two band systems by Kasha (1950). Out of the two, the system towards the shorter wavelength side has been attributed to $\pi-\pi$ transition and is also analogous to the 2600 A system of benzene. Ito (1976) and his coworkers were the first who systematically studied the electronic absorption and the Raman spectra of Pyridine and some of its deutrated analogue Due to the presence of two ($\pi-\pi$ and $n-\pi$) systems, Pyridine molecule has been a subject to experimental and theoretical investigation as regard substitution Spectroscopic studies on the electronic absorption, infrared and Raman spectra of some of the mono-substituted pyridines (1952, 1954, 1961, 1966, 1976) and few disubstituted pyridines (1973, 1974, 1978) by different workers are also available in the literature. With an aim to study the shift of the system together with the changes in the general features of the spectrogram as a whole by substituting strongly interacting groups/atoms, the present work has been undertaken. In each molecule only one elec-

tronic transition has been deciphered. The general features of the spectra in both the cases is identical to that of disubstituted benzenes. Both the molecules show bathochromatic shift of the 0, 0 band and the ν_1 mode appears strongly in each case. Therefore, on the basis of the above stated observations, it has been concluded that each spectra originates from π–π transition which is the shifted $^1A_{1g}$–$^1B_{2u}$ transition of benzene The absence of the n–π transition is probably due to the large inductive influence of the chlorine atom at 5-position in 5-Chloro-2-Pyridinol and at 2 position in 2-Chloro-3-Pyridinol on the nitrogen atom of the ring. In the absence of the informations like normal coordinate analysis, Raman shifts and vapour phase IR spectra, our assignment is tentative and is based on the group frequency approach together with the data available for similar molecules

2. Experimental

The vapour absorption spectra of the two molecules has been photographed on Hilger medium quartz spectrograph The low vapour pressure of the two compounds at room temperature necessitated the use of an absorption tube about one meter in length provided with heating coils. The temperature of the absorbing column was varied upto 150°C but large number of bands have been photographed around a temperature of 70°C in each case The bands in general are sharp in the spectra of 5-Chloro-2-Pyridinol and are broad in the spectra of 2-Chloro-3-Pyridinol. Sharp bands are accurate upto ± 5 cm^{-1} whereas this extends to ± 10 cm^{-1} in case of broad, weak and diffuse bands. The position of the bands in Å, and also in cm^{-1}, their separation from the 0, 0 band together with their assignment is presented in Tables 1 and 2 for the two molecules respectively The infrared absorption spectra of the two molecules have been recorded on Beckman IR-20 double beam spectrophotometer The position of the bands and their assignment is presented in Tables 3 and 4 for the two molecules respectively In each spectrogram, the bands in the region 400–2000 cm^{-1} are accurate to ± 10 cm^{-1} whereas in the region 2000–4000 cm^{-1} the order of accuracy is ± 20 cm^{-1}.

3. Discussion

Assuming OH group to be a mass point, the two molecules 5-Chloro-2-Pyridinol and 2-Chloro-3-Pyridinol may be ascribed to C_s point group. It has been pointed out earlier that each band system of the present investigation is shifted $^1A_{1g}$–$^1B_{2u}$ transition of benzene. Under the C_s point group the foresaid transition transforms to $^1A' \rightarrow {}^1A'$ which is an allowed one. The strongest band at 34261 cm^{-1} and at 35330 cm^{-1} towards the longer wavelength side of the spectrum appearing under the conditions of minimum vapour pressure inside the absorbing column has been classified as the 0, 0 band in 5-Chloro-2-Pyridinol and 2-Chloro-3-Pyridinol molecule respectively. The entire electronic spectrum in each

molecule has been analysed in terms of some ground and excited state fundamentals The vibrational spectra has been analysed in terms of fundamental vibrational frequencies, their combinations and overtone. Tables 5 and 6 presents the correlation of the fundamentals of the two electronic states together with their modal assignment for the two molecules respectively.

Table 1. Analysis of the $\pi-\pi$ transition of 5-chloro-2-pyridinol in the near ultraviolet region

Intensity	Position of the bands in A	Position of the bands in cm ^{1}	Separation from the 0.0 band in cm^{-1}	Assignment
w	2951·4	33872	0−389	0−389
w	2940·1	34004	0−257	0−257
w	2932·4	34092	0−169	0−2×85
mw	2929·0	34131	0−130	0−85−41
ms	2925·2	34176	0−85	0−85
ms	2921·4	34220	0−41	0−41
s	2917·9	34261	0, 0	0, 0 band
wd	2914 4	34302	0+41	0+41
mw	2911·7	34334	0+73	0+73
mw	2908·8	34368	0+107	0+366−257
m	2902·3	34445	0+184	0+568−389
w	2898·0	34495	0+235	0+271−41
ms	2895·0	34532	0+271	0+271
mw	2890·7	34584	0+323	0+366−41
ms	2887·1	34627	0+365	0+366
mw	2881·2	34698	0+437	0+825−389
w	2877·3	34745	0+484	0+568−85
w	2873·8	34787	0+526	0+568−41
ms	2870·3	34829	0+568	0+568
w	2866·6	34874	0+613	0+649−41
ms	2863·7	34910	0+649	0+649
w	2859·9	34956	0+695	0+2×366−41
ms	2857·0	34991	0+730	0+2×366

Table 1. (*Contd.*). Analysis of the $\pi-\pi$ transition of 5-chloro-2-pyridinol in the near ultraviolet region

Intensity	Position of the bands in A	Position of the bands in cm^{-1}	Separation from the 0 0 band in cm^{-1}	Assignment
mw	2852·1	35052	0+791	0+825−41
ms	2349·3	35086	0+825	0+825
w	2847·3	35111	0+850	0+934−85
w	2844 0	35151	0+890	0+934−41
m	2840·5	35195	0+934	0+934
m	2835·7	35254	0+993	0+1078−85
w	2832·3	35297	0+1036	0+1078−41
ms	2828·9	35339	0+1078	0+1078
wd	2823·6	35405	0+1144	0+366+825−41,2×568
m	2819 8	35453	0+1192	0+366+825
w	2811·1	35563	0+1302	0+366+934
w	2804·3	35649	0+1388	0+568+825
w	2798·0	35729	0+1468	0+649+825
m	2783·6	35914	0+1653*	0+2×285
w	2778·1	35981	0+1720	0+1078+649
m	2766·9	36131	0+1870	0+2×934
w	2764 6	36161	0+1900	0+1078+825
m	2757·0	36261	0+2000	0+1078+934
m	2744·9	36420	0+2159	0+2×1078

s = strong, ms = medium strong, m = medium, w = weak, d = diffuse.

(1) *Ring Vibrations*

The e_{1u} 1485 and e_{2g} 1596 cm^{-1} doubly degenerate mode of benzene represents the ring stretching vibration. These vibrations will split up into their components on the removal of degeneracy It is therefore expected that there will be four fundamental vibrational modes in each molecule. The pair of strong infrared bands at 1430 and 1465 cm^{-1} in 5-chloro-2-pyridinol and at 1430 and 1460 cm^{-1} in 2-chloro-3-pyridinol has been taken to represent the components of e_{1u} 1485 cm^{-1} mode of benzene. Similarly the pair of strong bands at 1540 and 1618 cm^{-1} in 5-chloro-2-pyridinol and at 1570 and 1600 cm^{-1} in 2-chloro-

Table 2. Analysis of the $\pi-\pi$ transition of 2-Chloro-3-Pyridinol in the near ultraviolet region

Intensity	Position of the bands in A	Position of the bands in cm^{-1}	Separation from the 0, 0 band in cm^{-1}	Assignment
wb	2855·9	35005	0−325	0 −325
wb	2849·3	35086	0−244	0 −510*+272
mb	2845·1	35138	0−192	0−550* +365
mb	2840·9	35190	0−140	0−510*+365
sb	2829·6	35330	0, 0	0, 0 band
mb	2818·8	35466	0+136	0+560−510*
wb	2814·1	35535	0+195	0+515−325
wb	2808·0	35602	0+272	0+272
mb	2800·7	35695	0+365	0+365
wb	2796·8	35745	0+415	0+970−550*
msb	2789·0	35845	0+515	0+515
msb	2778·5	35980	0+650	0+650
wb	2771·6	36070	0+740	0+2×365
mb	2766·4	36137	0+807	0+807
	2760·1	36220	0+890	0+365+515
mb	2754·0	36300	0+970	0+970
wb	2749·8	36356	0+1026	0+2×515
mb	2745·3	36615	0+1085	0+272+807
mbs	2739·4	36495	0+1165	0+1165
wb	2733·6	36571	0+1241	0+272+970
mb	2727·3	36655	0+1325	0+515+807
mb	2717·3	36790	0+1460	0+650+807
mb	2706·4	36939	0+1609	0+2×807
wb	2694.6	37100	0+1770	0+807+970
wb	2690·6	37103	0+1823	0+1165+650
wb	2680·1	37301	0+1971	0+1165+807

* Taken from the infrared spectra

s = strong m = medium w = weak b - broad ms = medium strong.

3-pyridinol has been identified as the compounds of e_{2g} 1596 cm^{-1} ring stretching mode of benzene.

The ν_1 a_{1g} 995 cm^{-1} and ν_{12} b_{1u} 1010 cm^{-1} mode of benzene represents the ring stretching and bending vibration respectively. Under the C_s point group both these fundamentals will have the same symmetry a'. Because of the same symmetry and small energy difference between these vibrations there exists a resonable amount of interaction which changes the energies of the two modes In the spectra of substituted benzenes the stretching mode reduces to a large amount depending upon the position, number, nature and the mass of the substituents whereas the changes in the bending mode are not very much appreciable. The absorption spectrum of 5-chloro-2-pyridinol and 2-chloro-3-pyridinol involves pair of intense excited state fundamentals 825 and 934 cm^{-1} and 807 and 970 cm^{-1} respectively. All the four vibrations have been found to be excited by two quanta except the 970 cm^{-1} mode The second quanta of this fundamental could not be traced because of the weak intensity of the bands in the region in which it is expected to be. The corresponding ground state frequencies in the two molecules could not be observed in the absorption spectrum because the spectrum towards the longer wavelength limits to only few bands under the best experimental condition. Due to this the pair of strong (900 and 1025 cm^{-1}) and (900 and 1050 cm^{-1}) infrared absorption bands have been chosen in the two molecules respectively for the purpose of the ground state values. These two vibrations have been taken to represent the totally symmetric ring stretching and bending modes of vibration of the two molecules. This assignment is in close agreement with those proposed for the similar molecules by Srivastava *et al* (1978) and Sanyal *et al* (1978).

Under the C_s point group the components of e_{2g} 608 cm^{-1}, the ring planar deformation mode, will appear separately. Spectral studies of substituted benzenes show that both the components are very much sensitive to the mass, nature and the number of substituents. Out of the two, the lower component reduces to a large amount as compared to the upper one

The strong bands at 34627 and 34829 cm^{-1} in 5-chloro-2-pyridinol and at 35695 and 35845 cm^{-1} in 2-chloro-3-pyridonol involves two pairs of (366 and 568 cm^{-1}) and (365 and 515 cm^{-1}) fundamentals in the two molecules respectively in the excited state. These vibrations are excited upto 2 quanta and combinations of these vibrations have also been observed in the spectra of the two molecules. It has been mentioned earlier thatbboth the band systems do not extend much towards the longer wavelength and due to this the corresponding ground state frequencies could not be observed. The pair of (505 and 616 cm^{-1}) and 510 and 550 cm^{-1}) intense infrared absorption bands in the spectra of the two

Table 3. Analysis of the infrared absorption spectra of 5-Chloro-2-Pyridinol

Position of the bands in cm^{-1}	Assignment	Position of the bands in cm^{-1}	Assignment
260 (vw*)	γ(C-Cl)	1482(m)	1100+380
380 (vw)	ν_{18}	1500 (sh)	
390(w)	γ(C-OH)	1510(sh)	
440 (vw)	ν_{16}	1540 (vs) } ν_8	
505 (vs)	ν_8	1618 (vs) }	
520 (vs)		1648 (vs*)	
616 (m)	ν_6	1657 (sh)	
620 (m)		1660 (sh)	
662 (vs)	ν(C-Cl)		
694 (w)	260+440	1748 (w)	1250+505
732 (w)	ν_4	1800 (vw)	2×900
815 (w)	440+380	1854 (vw)	1465+390
822 (m)	390+440	1900 (vw)	1230+662
830 (s)		2096 (vw)	1430+662
838 (vs)	$\nu_{16}\gamma$(C-H)	2230 (ms)	1618+616
900 (vs)	ν_1	2696 (m)	1465+1230
962 (ms)	$\nu_{17}\gamma$(C-H)	2795 (w)	1540+1250
985 (s)	$\nu_5\gamma$(C-H)	2845 (m)	1618+1230
1025 (w)	ν_{12}	2955 (m)	1618+1340
1100 (s)	ν_{20} β(C–H)	3036 (w) }	
1140 (s)	ν_{15} β(C–H)	3050 (w) }	ν (C–H)
1180 (m)	β(O–H)	3070 (w) }	
1230 (s)	ν_3 β(C–H)	3240 (w)	2×1618
1250 (ms)	ν (C–CH)	3460 (m)	ν (O–H)
1340 (vs)	ν_{14}		
1430 (vs)			
1465 (vs)	ν_{19}		

ν = stretching β = inplane bending γ = out of plane bending * Terms in this column show the intensity.

vs = very strong s = strong ms = medium strong w = weak, vw = very weak m = medium sh = shoulder. This band appear under higher concentration.

molecules has been taken to represent the ground state values. The above stated vibrations have been assigned as the components of e_{2g} 608 cm^{-1}, the ring planar deformation mode, in the spectra of the two molecules.

On the basis of the data available for the ring vibrations of substituted pyridines, the other vibrations are also dassigned and are listed in Tables 3 and 4 for the two molecules respectively.

Table 4. Analysis of the Infrared absorption spectra of 2-Chloro-3-Pyridinol

Position of the bands in cm^{-1}	Assignment	Position of the bands in cm^{-1}	Assignment
385 (w*)	ν_{16}	1295 (st)	ν_{14}
415 (vw)		1300 (s)	
510 (ms)		1356 (sh)	2×680
550 (ms)	ν_6	1380 (w)	2×690
680 (s)	ν_{11} γ(C-H)	1430 (w)	ν_{19}
690 (vs)	C-Cl stretching	1452 (sh)	
720 (s)	ν_4	1460 (vs)	ν_{19}
790 (vs)	ν_{10} γ(C-H)	1465 (sh*)	
795 (sh)		1486 (w)	790+690
900 (ms)	ν_1	1570 (vs)	ν_8
965 (w)	ν_{17} γ(C-H)	1600 (ms)	
1040 (vw)		1710 (vw)	1300+415
1050 (w)	ν_{12}	2600 (vw)	1300×2
1060 (s)		2700 (vw)	1430+1270
1080 (m)	690+385	2720 (m)	1430+1300
1092 (m)	680+415	2740 (m)	1570+1172
1100 (s)	ν_{20} β(C-H)	3030 (vw)	ν(C-H)
1125 (sh)		3095 (vw)	
1172 (s)	ν_9 β(C-H)	3460 (w)	ν(O-H)
1190 (s)	β(O-H)	3610 (m)	3095-510
1208 (ms)	690+510	–	
1248 (ms)	ν_3 β(C-H)		
1270 (s)	C-OH stretching		

* Terms in this column show the intensity.
vs = very strong, s = strong, ms = medium strong, w = weak,
vw = very weak, m = medium and sh = shoulder
β = inplane bending, γ = out of plane bending.

(ii) *C–H Vibration*

The molecules under consideration are di-substituted pyridines Due to this there are only three hydrogen atoms which are attached to the ring at various positions in the two molecules. These three C–H bonds will involve 3 C–H stretching, inplane and out of plane bending vibrations.

It has been pointed out by Bellamy (1959) that multiple absorption bands in the vibrational spectra of pyridine in the region 3020–3070 cm^{-1} are due to CH stretching vibration. In the spectra of 5-chloro-2-pyridinol all the three CH stretching vibrations have been identified at 3036, 3050 and 7070 cm^{-1} but in 2-chloro-3-pyridinol due to the weak intensity of the absorption bands in this region only two bands have been deciphered and are listed in Table 4

On the basis of the data available for substituted pyridines, the inplane and out of plane C–H vibrations in each molecule are assigned and are presented in Table 3 and 4 respectively.

(iii) *C–OH stretching and OH in plane deformation mode*

It has been pointed out by Kletz and Price (1947) that in substituted phenols there occurs a strong band around 1300 cm^{-1} Further it has been suggested by these workers that it corresponds to a mode involving the valence oscillation of the OH group to the ring.

It has been suggested by Bellamy (1959) that OH deformation mode occurs near 1200 cm^{-1}. This argument is supported by many other workers also. On the basis of the argument given by Kletz and Price C–OH stretching mode

Table 5. Correlation of the infrared and ultraviolet absorption frequencies of 5-Chloro-2-Pyridinol and their assignment to probable modes

Infrared frequencies	Ultraviolet absorption		Modes of vibration
	Ground state cm^{-1}	Excited state cm^{-1}	
260	257	—	C-Cl non planar bending
390	339	271	C-OH non planar bending
505	—	366	Components of e_{2g} 608
616	—	568	mode (ν_6 mode)
662	—	649	C-Cl stretching
900	—	825	Ring stretching (ν_1 mode)
1025		934	Ring bending (ν_{12} mode)
1250		1078	C-OH stretching

absorbs at higher frequencies under the influence of the ring. There are, therefore, possibilities of coupling between OH and C–OH frequency or between the C–OH frequency and the ring. Mecke and Rossmy (1955) have made an assignment in which they regard the 1180 cm^{-1} band of phenol as being that which possesses the strongest OH character. On the basis of this argument together strongest band at 1250 and 1180 cm^{-1} in 5-chloro-2-pyridinol and at 1270 and 1190 cm^{-1} in 2-chloro-3-pyridinol has been assigned as the C–OH stretching and O–H in plane bending vibration.

Table 6. Correlation of the infrared and ultraviolet absorption frequencies of 2-Chloro-2-Pyridinol and their assignment to probable modes

Infrared frequencies	Ultraviolet absorption		Modes of vibration
	Ground state cm^{-1}	Excited state cm^{-1}	
—	325	272	C-Cl non-planar bending mode
510	—	365	Components of c_{2v} 608
550		515	mode (ν_6 mode)
690		650	C- Cl stretching
900		807	Ring stretching (ν_1 mode)
1050		970	Ring bending (ν_{12} mode)
1270		1165	C-OH stretching

Shift of the 0, 0 *band*

The 0, 0 band of the π–π system of pyridine appears at 38350 cm^{-1} in vapour state. The analysis of the electronic absorption band system of 5-chloro-2-pyridinol and 2-chloro-3-pyridinol shows the presence of 0, 0 band at 34261 and 35330 cm^{-1} in the two molecules respectively. It appears that the band system of the two molecules has shifted towards the longer wavelength by 4089 and 3020 cm^{-1} respectively. On the basis of this red shift together with the strong appearance of the ν_1 mode in each case it has been concluded that both the band system originates from π–π transition.

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